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DETERMINING, WITH THE AID OF A SPECTROPHONE, THE SPEED OF TRANSITION
OF MOLECULES' OSCILLATORY ENERGY TO THE ENERGY OF FORWARD MOTION

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"DETERMINING, WITH THE AID OF A SPECTROPHONE, THE SPEED OF TRANSITION OF MOLECULES' OSCILLATORY ENERGY TO THE ENERGY OF FORWARD MOTION."

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The problem of the speed of transformation of the oscillatory energy of molecules of gas into their energy of forward motion possesses real significance. Up to the present time, however, almost no pertinent measurements have been carried out. What we are interested in is the lapse of time in which the energy of intramolecular oscillation, arising as a result of the absorption, by a molecule, of a suitable infra-red quantum, is transformed, or converted, by way of inelastic collision into the energy of forward motion. Hereafter this quantity we shall call, for the sake of brevity, "The existence time of an oscillatory quantum".

In 1931 Knauer determined, by an indirect method based upon a study of sound dispersion, this time for the 14.8 micron band of CO_2 (vide Ann. der Phys. 11, 777). In 1942 A. N. Terenin and G. G. Neuymin determined the existence time of a quantum corresponding to the radiation band 4.8 microns in CO_2 (vide Iz. AN SSSR, OKhN, 5, 246). The calculation was based upon an analysis of the processes taking place in this gas during discharge. In 1946 G. S. Gorelik showed that the optico-acoustic phenomenon, based upon the operation of the spectrophone, can be employed to determine this quantity by way of the investigation of the frequency dependence of amplitude or phase of pressure in the optico-acoustic phenomenon (vide Doklady 54, 783).

During measurements, with the aid of his spectrophone, of the intensity of infra-red absorption bands of CO_2 , Veyngerov discovered another possibility, different from the method proposed by G. S. Gorelik, namely the possibility

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of measuring by this apparatus the existence time of oscillatory quanta (vide M. L. Veyngerov, Doklady 46,200, 1945). As a result he worked out a method that permits one to measure the existence time of quanta by direct means without the introduction of indirect considerations, for all gases and vapors that possess infra-red absorption bands. With the aid of the method developed, measurements were made of the existence times of oscillatory quanta that (times) correspond to the following three absorption bands in CO_2 : 2.7, 4.3, and 14.8 microns. Moreover, it turned out possible to determine the dependence of existence time upon the concentration of absorbing molecules and to reveal that non-absorbing air influences the existence time much more weakly than CO_2 molecules.

The construction of the spectrophone and its principle of operation are explained in Figure 1 (all Figures are in the Appendix). The flow of radiation emitted by source 1 (Nernst's) is directed by spherical mirror 2 to entrance aperture 3 of reflecting monochromator 4 supplied by removable prisms, namely, sylvite and fluorite. The monochromator (of M. A. Yur'yev and I. A. Tel'tevskiy's design) isolates the region of the infra-red spectrum that (region) corresponds to absorption band being studied (Vide Iz AN SSSR Ser. Fiz 11,452, 1947). The outlet aperture 6 in this work was such that it sets free the spectral region that completely encloses the absorption band subject to investigation. Immediately in front of the entrance aperture is a revolving disk 5. (The disk has 6 teeth and 6 gaps; the diameter of the disk is 180 mm and the width of the teeth and gaps is 45 mm.) The speed of revolution of the disk is such that the frequency of interruption equals 250 cycles. After spectral refraction the radiation from outlet aperture 6 enters optico-acoustic chamber 7, which is filled with a mixture of CO_2 under study and air. The optico-acoustic chamber possesses

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the structure as represented in Figure 2 (in the Appendix). In its lower cylindrical part 8 is placed microphone 9, whose outlets pass through ebonite collars inserted in the cap 10. The upper part of the chamber 11 is a horizontally disposed cylinder; the filling of the gas-air mixture is carried out through stopcocks 12 and 13. The infra-red radiation enters the chamber through sylvite window 14 and passes through a layer of gas 5 cm thick to pass out through window 15. The radiation passes through the gas without falling upon the walls of the chamber. In order to shield as much as possible the microphone from internal noises, the chamber is suspended on rubber suspenders; moreover, it is located ~~in~~ located in a massive iron case supplied with a thick aperture, or window. The iron protects at the same time the microphone from electro-magnetic induction. The electromotive force developed by the microphone as a result of the optico-acoustic phenomenon is ^{amplified} ~~strengthened~~ by a two-tube amplifier 16 (Figure 1) and is measured by a direct-current mirror galvanometer 17.

In order to be able to carry out measurements with aid of the direct-current apparatus, it is necessary to convert the variable signal at the output of the amplifier into intermittent current of constant voltage. This is done with the aid of a mechanical interrupter or breaker 18. The interrupter to the spectrophone, as developed by Veygerov, consists of a revolving motor 19 (Figure 1) for a cubic prism, to which a small hammer is pressed by a spring - the hammer being thrown out six times each revolution of the prism. The hammer is thrown out from a contact, as a result of which the circuit containing the galvanometer is interrupted. The disk is located on one axis with the interrupter so that the interruption of the light and of the contact proceed in perfect synchrony; the time for closing contact equals the time of opening.

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By adjusting the disk in various positions relative to the contact apparatus one can move in any manner the moment of occurrence of radiation into the chamber from the moment of closing of the contact. The interrupter will let pass through the galvanometer that part of the period of the variable signal, occurring (signal) in the output of the amplifier, which (period) coincides with the time of closing. It is possible to adjust the disk relative to the contact in such way that the time of closing will correspond to either just positive or just negative semiperiods of the variable signal at the output of the amplifier (Figure 3a). It is possible to adjust the disk so that the time of contact has corresponded to two unequal parts of adjacent semiperiods (Figure 3b); then the readings of the galvanometer will be less than in the first case. Finally, it is possible to adjust the disk relatively to the contact apparatus so that in the interval of closing two equal parts of adjacent semiperiods appear (Figure 3c); in this case the galvanometer will not deflect at all. The magnitude of displacement of the disk relative to the contact, corresponding (magnitude) to the last case, would not depend upon the concentration of the absorbing gas in the air and upon the absorption band, if the oscillatory energy of the molecules, stored by them during absorption of the corresponding quanta at the time of occurrence of radiation into the chamber, were converted into the energy of forward motion always with the same speed.

It was discovered, however, that the displacement of the disk relative to the contact depends upon both of the enumerated factors.

If, in the optico-acoustic chamber in which is located a mixture of CO₂ and air, the flow of radiation of 2.7 micron wavelength corresponding to one of the gas' absorption bands is adjusted, from the start, from the monochromator, so that galvanometer does not deflect, but after that is adjusted into the chamber to the radiation with wavelength 4.3 microns

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corresponding to another absorption band of CO_2 , - then the galvanometer is deflected from its zero position. In order, in this case, that the galvanometer does not deflect, it is necessary to shift the disk to another position. This can be explained by the different duration of the existence time of oscillatory quanta corresponding (quanta) to these two absorption bands. By knowing the frequency of interruptions of radiation and also the angle to which it turned out necessary to shift the disk relative to the contact, one can determine how much longer one quantum exists than another. By studying the dependence of the disk's angle of turn relative to the contact upon concentration, one can, it turned out, find the absolute magnitude of the duration of existence of the quanta.

Results of Measurements:

Figure 4 shows the results of measurements for the following absorption bands of CO_2 : 4.3 microns - curve 1; 2.7 microns - curve 2; and 14.8 microns - curve 3. The differences in the ordinates of curves 1, 2, and 3 equal the differences in the existence times, expressed in seconds. It is evident that the differences in times diminishes in proportion to the increase in the concentration of the absorbing CO_2 molecules.

In order to determine the absolute magnitude of the existence times of the quanta it is necessary to turn our attention upon the fact that the curves approach asymptotically to a certain straight line parallel to the abscissa axis. (Note: The graph is discontinuous for a concentration of 34% CO_2 . The measurement succeeding after a concentration of 34% was carried for 100%. At this concentration one value of the ordinate corresponds to all three bands; therefore, in the limits of absorption the measurement does not differ from the ordinate for 34%; that is, it practically lies on the asymptote.) This straight line intersects the ordinate axis at $t = e$.

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This conclusion proceeds from the following considerations: The slowly falling portion of the curves are expressed very well by a hyperbolic dependency (curve 1a); by small crosses in the circles we note the points obtained by way of calculations according to a hyperbolic law, if the value of one of the experimental points, for example at 10%, takes on unity.

The hyperbolic dependence is explained by the fact that the existence time of quanta is inversely proportional to the number of collisions of an excited molecule ^{with} the surrounding molecules. Keeping in mind that the collisions occur both with molecules of the same absorbing gas and with the molecules of the air and that the effectiveness of the last collisions in the sense of a break or discontinuity in existence of a quantum can be different from the effectiveness of collisions with CO₂ molecules, we see that the average existence time of a quantum can be written as in the following expression:

$$t = \frac{1}{a\bar{n}_1 + b\bar{n}_2}$$

where the number of collisions of excited molecules with CO₂ molecules is designated by \bar{n}_1 , and with air molecules by \bar{n}_2 ; a is the coefficient that determines the number of elastic collisions with CO₂ molecules occurring for one nonelastic collision which (collision) converts an oscillatory quantum unto forward energy; b is a similar coefficient, relating to collisions with air molecules.

When the CO₂ concentration is increased, the $b\bar{n}_2$ term tends toward zero and the formula transforms in the following expression:

$$t = \frac{1}{a\bar{n}_1}$$

Consequently the existence time of a quantum is inversely proportional to the number of CO₂ molecules per unit volume; if the density of CO₂ increases infinitely great^{ly}, the existence time tends towards zero; consequently the point of intersection of the straight line, which is the asymptote of the hyperbolic portions of the experimental curves, with the ordinate axis is the origin of the absolute calculation of existence time.

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In the region of concentrations less than 5%, a notable absence or departure from hyperbolic dependency begins to set in. This can be explained by the fact that in the expression for t it is still impossible to neglect the term bs_2 . In order to evaluate the relation between coefficient a and coefficient b it is necessary to compare the ordinate of the experimental curve with the ordinate of the hyperbola⁺ for example, at a concentration 0.5%.

From comparison it is evident that the ordinate of the hyperbola is roughly two times greater than the ordinate of the experimental curve; that is, that 0.5% of the CO_2 gas has the same influence on the existence time of a quantum as 99.5% of air. Hence it is obvious that collisions of excited CO_2 molecules with air molecules is 200 times less effective than collisions with CO_2 molecules. This pertains to bands 4.3 and 2.7 microns. A conclusion concerning the relation between the coefficients a and b for the band 14.8 microns is still impossible to make since in this case measurements for sufficiently small concentrations were not carried out.

The table gives the results of measurements of the existence time of quanta for various concentrations. In the right column are shown the probabilities of inelastic collisions; that is the share of inelastic collisions relative to one elastic collision.

The accuracy of measurement of the existence times of quanta for the bands 4.3 and 2.7 microns in one series of measurements averaged 10%.

The value obtained for the existence time of a 4.3 micron quantum compares successfully with the value obtained by A. N. Terenin and G. G. Neuymin in analyzing the kinetics of the excitation process of oscillatory bands radiated by CO_2 during discharge.

The results obtained by Kneser with the aid of a study of sound dispersion for 14.8 microns in CO_2 differ slightly from our results. He found that the existence time for the band 14.8 microns is 10^{-6} second, but in our work it proves to be equal to 1.6×10^{-6} second.

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It should be pointed out that the maximum observed values of existence time permit us to evaluate the lower limit of the average time, which (time) determines the spontaneous radiation, for the band 4.3 micron as equal to 6×10^{-4} second and for the band 2.7 microns as equal to 3×10^{-4} second.

This follows from the fact that if spontaneous transitions that are accompanied by radiation were to proceed ^{much} faster, than a sound would not arise in the optico-acoustical chamber. (vide M. L. Veyngerov, Zaved. Labor. 13, 426, 1947).

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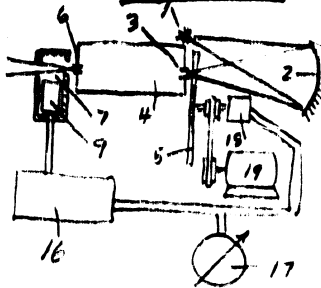
(Figures appended)

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Appendix **CONFIDENTIAL**

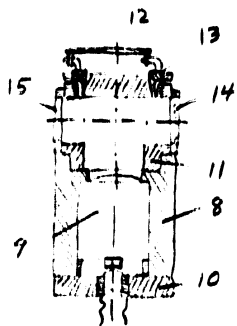
Figure 1



Scheme of the spectrophone:

- 1- source of radiation.
- 2- spherical mirror.
- 3- entrance aperture.
- 4- mirror monochromator.
- 5- rotating disk
- 6- outlet aperture.
- 7- optico-acoustic chamber.
- 9- microphone.
- 16- amplifier.
- 18- interrupter, or breaker.
- 19- motor.

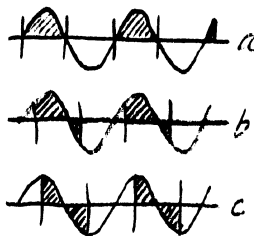
Figure 2



Scheme of the optico-acoustic chamber:

- 8- cylindrical part of the chamber.
- 9- microphone.
- 10- cap.
- 11- upper part of the chamber.
- 12, 13- taps.
- 14, 15- windows.

Figure 3



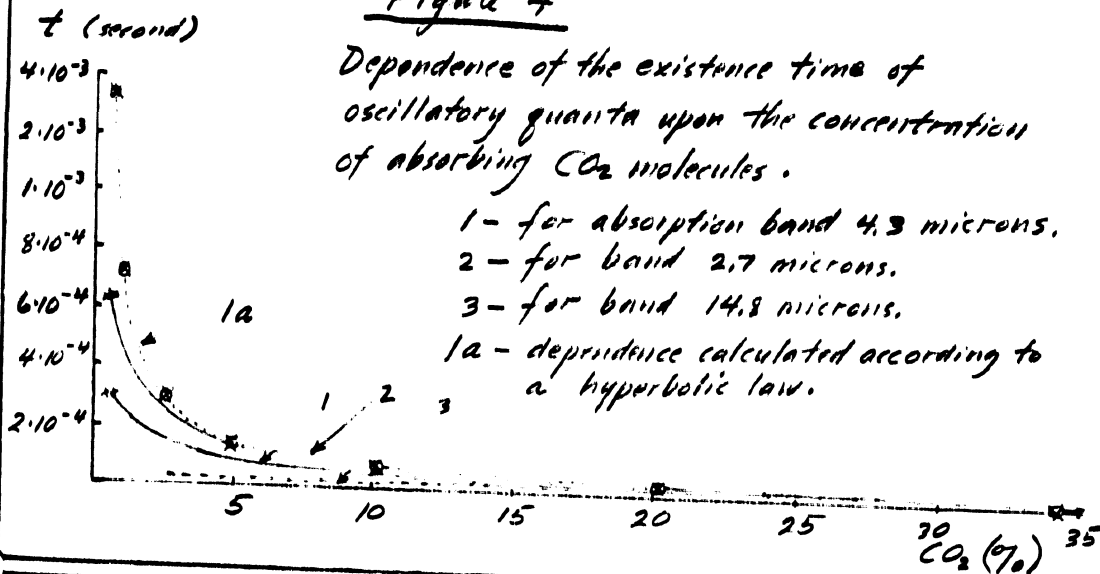
Scheme showing the relation between the interval of closing of the contact of the interrupter (cross-hatched) and the period of variable signal at the output of the amplifier.

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Figure 4

Dependence of the existence time of oscillatory quanta upon the concentration of absorbing CO_2 molecules.



Table

The Existence Time of Quanta for Various Concentrations of CO_2

λ, μ	0.4	0.7	1.1	2.2	3.6	5.4	7.3	9.8	17.0	100*	** P
4.3	$6 \cdot 10^{-4}$	$6 \cdot 10^{-4}$	$3.7 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$7 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$7 \cdot 10^{-5} \text{ sec}$	1.6×10^{-5}
2.7	$3 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$4 \cdot 10^{-5} \text{ sec}$	2.8×10^{-5}
14.8	—	—	—	$5 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	—	$2 \cdot 10^{-5}$	—	$1.6 \cdot 10^{-5} \text{ sec}$	6.9×10^{-5}

* Note: The value of the existence time for 100% concentration is obtained by way of extrapolation, using a hyperbolic law, since the experimental point for this concentration lies, in the limits of error, on the asymptote.

** Note: P is the probability of inelastic collisions.

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-10- (END OF APPENDIX)